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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

*Standard Reference Materials:*

## **SRM 1470: POLYESTER FILM FOR OXYGEN GAS TRANSMISSION MEASUREMENTS**

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## Standard Reference Materials:

# SRM 1470: POLYESTER FILM FOR OXYGEN GAS TRANSMISSION MEASUREMENTS

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# TABLE OF CONTENTS

|   | <u>Page</u> |
|---|-------------|
| 1. Introduction . . . . .   | 2           |
| 2. Selection of a Film for Use as an SRM for Oxygen Gas Transmission Rate . . . | 3           |
| 2.1 SRM 1470 - Provenance and Packaging . . . . .                               | 4           |
| 2.2 Sampling for Characterization Purposes . . . . .                            | 5           |
| 2.3 Treatment of Specimens Prior to Testing . . . . .                           | 5           |
| 3. Data Collection for Certificate Values . . . . .                             | 6           |
| 4. Statistical Analysis of the Experimental Data . . . . .                      | 9           |
| 4.1 Models for Describing the Experimental Data . . . . .                       | 9           |
| 4.2 The Significance of the Regression Estimates . . . . .                      | 10          |
| 4.3 Specimen-to-Specimen Variability . . . . .                                  | 12          |
| 5. The Accuracy of the Mean Values of $P$ and $\tau$ . . . . .                  | 16          |
| 5.1 Variances of the Mean Values . . . . .                                      | 18          |
| 5.2 The Use of SRM 1470 in Interlaboratory Comparisons . . . . .                | 18          |
| 6. How to Use the Certificate Values for SRM 1470 . . . . .                     | 21          |
| 7. The Units of $P$ . . . . .   | 22          |
| 8. Miscellaneous Aspects of SRM 1470 . . . . .                                  | 23          |
| 8.1 Effect of Thermal History ("Aging") . . . . .                               | 23          |
| 8.2 Significance of the Leakage Flux . . . . .                                  | 25          |
| 8.3 Glass Transition Behavior in SRM 1470 . . . . .                             | 26          |
| 8.4 Another Method for Assessing Pinholes . . . . .                             | 26          |
| 9. Corrections for Non-Standard Temperature and Pressure . . . . .              | 28          |
| 10. Acknowledgements . . . . .  | 29          |
| 11. References . . . . .  | 30          |
| 12. Appendix A . . . . .  | 32          |

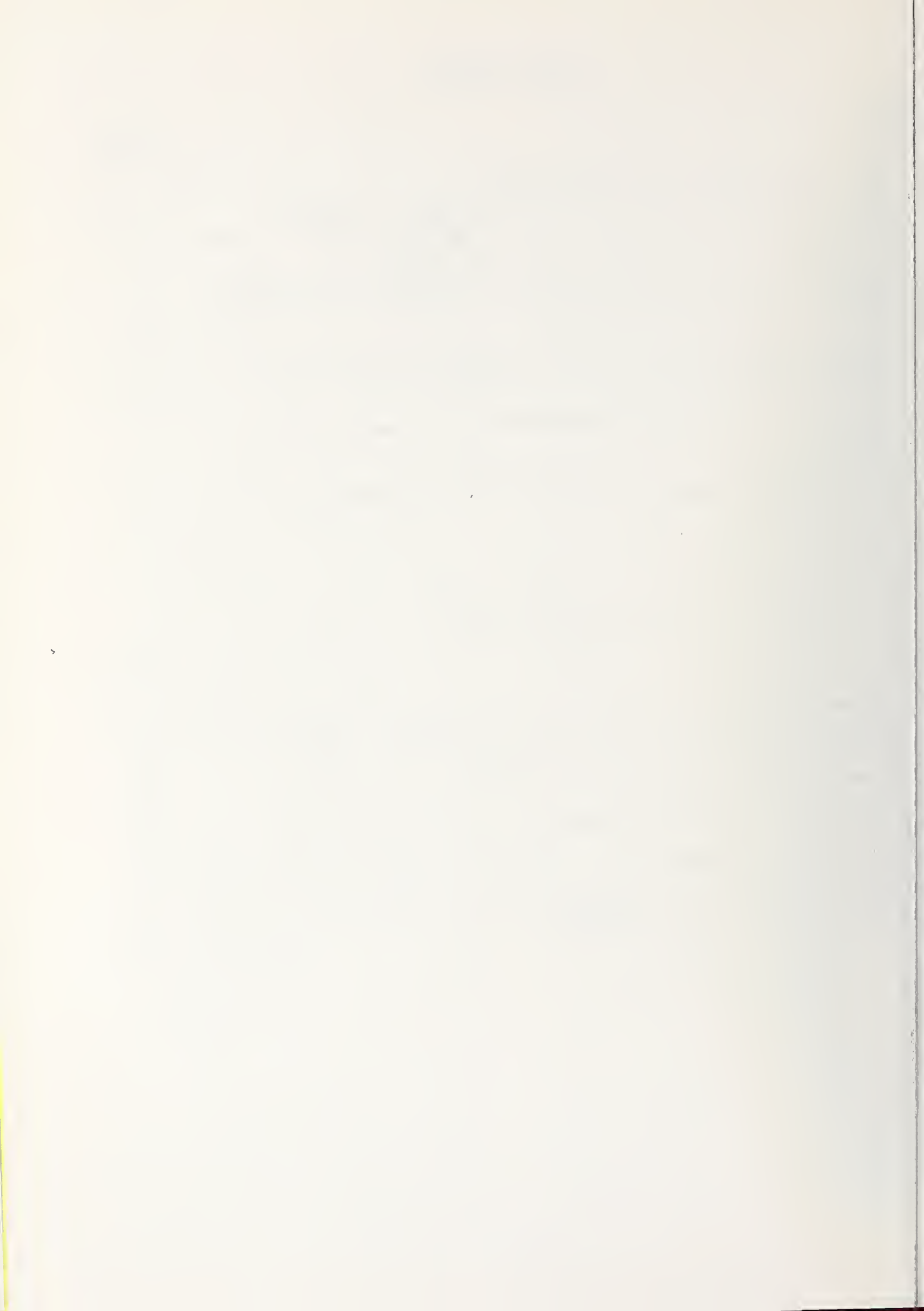


## LIST OF FIGURES

| Figure   | <u>Page</u> |
|--|-------------|
| 1. Cross Sectional View of the NBS Sample Cell . . . . .   | 8           |
| 2. Scatter Diagram for the Specimen Effect on the Measured Permeance . . . . .   | 13          |
| 3. Scatter Diagram for the Specimen Effect on the Time-Lag . . . . .   | 13          |
| 4. Scatter Diagram Giving Specimen Effect on the Permeance as a Function of<br>Position Within the Stratified Sample . . . . . | 14          |
| 5. Scatter Diagram for Time-Lag Values as a Function of Position of the<br>Specimen Within the Stratified Sample . . . . .     | 14          |
| 6. Correlation Plot of the Specimen Effect for Permeance Versus that for<br>Time-Lag . . . . .                                 | 17          |
| 7. DSC (Differential Scanning Calorimetry) Thermogram for SRM 1470 . . . . .   | 27          |

## LIST OF TABLES

| Table  | <u>Page</u> |
|--|-------------|
| 1. Treatment Schemes Used to Measure Certificate Values for SRM 1470 . . . . . | 6           |
| 2. Estimates from Multiple Linear Regression Analysis . . . . .                | 11          |
| 3. Differences Between Samples from the Same Can . . . . .                     | 16          |
| 4. Quantities for Interlaboratory Comparisons . . . . .                        | 19          |
| 5. Units Related to Permeability . . . . .                                     | 21          |
| 6. Effect of Thermal History on Permeability . . . . .                         | 24          |
| 7. Effect of Thermal History on Time-Lag . . . . .                             | 25          |





SRM 1470: Polyester Film for Oxygen Gas Transmission  
Measurements

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Abstract

This report presents information which should be of interest to users of NBS Standard Reference Material 1470. This SRM takes the form of 23  $\mu\text{m}$  thick sheets of poly(ethylene terephthalate) film. The gas transmission rates of these films with respect to oxygen gas have been carefully analyzed. We describe where the film comes from, how it is packaged, and how it should be conditioned prior to measuring. The steps which were taken to characterize a random sample of sheets from the production lot of the SRM are discussed in detail. The gas transmission rates and the time-lags of 22 films were measured using a state-of-the-art electronic manometric permeation facility. The temperature dependence of the permeability was determined over the temperature range 288 K to 310 K. A small pressure effect was found which is thought to be an artifact. The statistical measures which were derived from the data are discussed in detail. It is concluded that the largest source of variability is from one sample to another with a coefficient of variation amounting to 4 percent. A brief discussion of units for expressing permeabilities is given. Effects due to thermal conditioning ("aging") and outgassing are discussed.

Key Words: Gas transmission rate; manometric technique; oxygen; permeability; poly(ethylene terephthalate); standard reference material; temperature coefficient; time-lag.

## 1. INTRODUCTION

The oxygen gas transmission characteristics of polymer films used in packaging are frequently a primary determinant of the performance of packages made from such films. Films which do not allow gases or vapors to permeate them are said to have good "barrier properties." In the packaging industry there are cases where good barrier properties are desirable and other cases where a film with poor barrier properties is desirable. The role of oxygen gas or water vapor [1,2]<sup>1</sup> in causing premature degradation of food or drug products is obvious. Less obvious is the role that a controlled influx of oxygen can play in maintaining the appearance ("bloom") of packaged meats [1]. There are a number of applications of packaging materials in which films of two or more materials are laminated to produce barriers with special properties. In all such applications it is necessary to have means of monitoring the performance of the barrier materials.

Early in 1975, members of ASTM Committees F-2 (Flexible Barrier Materials) and D-20 (plastics) decided that there was a need to undertake the development of standards relating to the use of a commercially available measurement system for oxygen gas transmission rates which is based on a coulometric detection principle [3]. In order to evaluate the precision and accuracy of such measurements it was necessary to have available, for interlaboratory testing, a quantity of a barrier material with known oxygen gas transmission properties. The similarity between this requirement and the criteria for establishment of a Standard Reference Material (SRM) [4] led the Polymers Division to undertake studies aimed at the establishment of suitable SRM's. A market survey revealed that there was likely to be enough demand on a continuing basis to justify SRM production.

Once the desirability of an oxygen gas transmission SRM was established, the three primary technical questions which had to be answered were:

- 1) What properties of the SRM should be measured in order to meet the user's needs?
- 2) What substance possesses the most desirable properties for consideration as an SRM?
- 3) What is the state of the art needed to measure the desired characteristics of the SRM?

In order to answer the first of these questions, let us consider a description of transport of one substance through a matrix of a different substance [5]. We assume at the outset that transport in a homogeneous membrane is described by values of the diffusion coefficient,  $D$ , and the solubility,  $S$ , which are independent of permeant concentration and position within the matrix. We further assume that there is a linear relationship between the external vapor pressure,  $p$ , and the equilibrium concentration,  $C$ , within the matrix (Henry's Law;  $C=Sp$ ). If we consider a membrane of thickness  $\ell$  with a pressure  $p_1$  on one side and a pressure  $p_2$  ( $p_2 < p_1$ ) on the other side then gas will be transported across a unit area of the membrane at a rate

---

<sup>1</sup>Numbers in square brackets refer to the list of references at the end of this paper.



$$F = \frac{DS}{\ell} (p_1 - p_2) = P(p_1 - p_2) \quad (1)$$

It is this rate of gas transmission,  $F$ , which is the quantity of interest to workers in the packaging industry. In general,  $p_1$  is the partial pressure of the chosen permeant species in the atmosphere and  $p_2$  is zero. The combination of  $D$ ,  $S$ , and  $\ell$  can be measured more accurately than any single component (see reference [6] for further discussion of this question). For this reason, we elected to characterize  $P$ , the ratio between the permeant flux and the partial pressure difference across the membrane. We call this quantity the "permeance."

If the experiment to characterize the permeance<sup>2</sup> is properly carried out, it is possible to characterize an additional quantity  $\tau$ , called the "time-lag." Under the assumption of a homogeneous membrane the time-lag is given by  $\tau = \ell^2/6D$  [5]. The time-lag is a measure of the length of time required for the permeant flux to reach a steady state after a step-function increase in the pressure is applied to the upstream side of a membrane which is free of permeant. As will be discussed later, the time-lag is a useful tool in checking for pinholes in films.

The temperature and pressure variation of both the permeance and the time-lag should be characterized so that meaningful comparisons between measurements can be carried out over a range of temperatures and pressures rather than at just one set of conditions.

Our examination of the existing permeation measuring methods demonstrated that the best way to obtain a system with the required sensitivity, flexibility, and traceability was to build it ourselves along classical lines [7]. The result was an automated partition cell using a capacitance-operated manometer as the detector. The development and use of this instrument are described elsewhere [6].

## 2. SELECTION OF A FILM FOR USE AS AN SRM FOR OXYGEN GAS TRANSMISSION RATE

Five characteristics which an SRM should possess are listed below:

- 1) The material should be homogeneous with respect to the property of interest throughout a lot.
- 2) The size of the lot should be large enough to permit all interested parties to obtain samples for a period of ten years or so.
- 3) The material should be stable under storage and shipment during the period it is stocked.
- 4) It should be possible to fabricate test specimens without changing the characteristics of the material.

<sup>2</sup> In the certificate for SRM 1470 (see Appendix A) this quantity is called the "permeability coefficient." The matter of units is discussed more fully in Section 7.

- 5) The material should possess a value of the parameter under test which is representative of the range of the apparatus used in industry to measure the property.

A sizable segment of the packaging industry has already adopted poly(ethylene terephthalate) (PET) film approximately 25  $\mu\text{m}$  in thickness as a de facto standard. In many ways this is an excellent choice. The material is plentiful, thus guaranteeing an assured supply. Dimensional stability at ambient temperature is good, indicating that any annealing effects [8] are taking place very slowly. Some annealing effects may be detectable over a long period of storage.

PET is a "good" oxygen barrier. "Excellent" oxygen barriers possess gas transmission values approximately 1/5 to 1/50 of the ones for PET. It is thought that the barrier properties of PET are relatively insensitive to the presence of moisture or other extraneous influences but our knowledge in this area is inadequate. A limited attempt to estimate the effect of "aging" on the film was made in the present study (see Section 7.1). It is known that "cyclic trimer" and other low-molecular-weight species are present in the material and the effect of these on the aging process or the barrier properties is poorly known.

PET film in the 25  $\mu\text{m}$  thickness range is relatively robust. Care must be taken to avoid creasing the film as this is likely to produce pinholes. The usual dies, punches, etc. can be used to cut out samples for measurement.

No other candidate film which was clearly superior to PET with respect to the above characteristics was offered for consideration and it was decided to use a 23  $\mu\text{m}$  PET film on the basis of past experience.

## 2.1 SRM 1470 - Provenance and Packaging

The polyester film from which SRM 1470 is made was obtained from E. I. DuPont de Nemours and Company<sup>3</sup> in the form of sheets approximately 21 x 27 cm with a nominal thickness of 23  $\mu\text{m}$ . The film is known to be biaxially drawn and has a nominal density of 1395  $\text{kg/m}^3$ .

The roll from which the sheets are cut is the middle third of a mill roll. Experience shows that the middle third is more uniform in thickness and has fewer flaws than the outer parts. The roll of film was cut into sheets and stacked by a machine whose operation is such that every fifth sheet in the stack came from an adjoining part of the roll.

The sheets of film were packaged by NBS for distribution before the specimens used in the random sample were drawn. Fifteen sheets of film are packaged in a cylindrical tinplate can approximately 10 cm in diameter and 25 cm long. The can has a friction fit lid. The fifteen sheets were simply taken consecutively from the lot of material as received. Special care was taken to avoid creasing the film at all stages of the packaging and other handling. The packet of fifteen sheets is enclosed in a slip case made from a high quality paper with a low pH and a low sulphur content. This slip case is intended to protect the film from damage caused by the metal can or the hands of the user.

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<sup>3</sup>Identification of the products of particular manufacturers is made purely for purposes of identifying experimental conditions and does not imply endorsement by the National Bureau of Standards.



## 2.2 Sampling for Characterization Purposes

Two goals of the experimental work were to provide characterization of the "true" mean value of the permeability coefficient in the lot of material which makes up SRM 1470 and to provide meaningful measures of the variability that a user could expect from measurements on individual sheets of film or from different films within the small lot of fifteen sheets issued by NBS.

A stratified random sample was chosen as the scheme for selecting films from the lot for testing. This procedure offered the prospect of being able to characterize systematic variations from one part of the lot to another. The scheme for sampling was as follows:

- 1) The population of 1120 cans of film was divided into 28 sequential groups of 40.
- 2) One can of the 40 was selected at random from each group.
- 3) Two films out of the fifteen in each can were selected at random. Thus, there were a total of 56 samples.
- 4) The samples were numbered from 1 to 56.
- 5) The order in which the samples were submitted to testing was determined with the help of a random number table.
- 6) Measurements were terminated when enough degrees of freedom had been accumulated to adequately characterize the population of SRM films.

## 2.3 Treatment of Specimens Prior to Testing

Other workers have found that better results are obtained if films are preconditioned before their gas transmission rate is measured. Care must be exercised in choosing proper conditions because it is possible to change the crystallinity of PET by annealing it at temperatures not too far below its glass transition [8] ( $75\text{ }^{\circ}\text{C} < T_g < 95\text{ }^{\circ}\text{C}$ ). We observed that the films tend to outgas over long periods of time. This tendency is somewhat reduced if the film has been placed under a vacuum at a temperature in the neighborhood of 40 to 50  $^{\circ}\text{C}$  (i.e., well above the actual measurement temperature). The experimental results in Section 8.1 indicate that the effect of thermal history on the permeation rate as measured by our method is small. It is possible that the leakage or background flux, which is found to be strongly influenced by prior conditioning, interferes with measurements in some cases. Those outgassing species which are removed by this rather mild treatment are probably atmospheric gases such as  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. There is another, much more tenacious, component which is probably made up mainly of low-molecular weight degradation products or oligomers of PET.

During a measurement, there is additional outgassing because the gas is in contact with the specimen only while measurements are actually being made. There may be delays of from 2 to 8 hours between the time a fresh specimen cell is connected to the system and the first measurements are made.

Users who make measurements within a short time after placing the specimens in their measuring apparatus should expect short-term drifts. This is likely to be true in any non-specific detection scheme where correction is not made for the background flux.

In order to be on the safe side and since we found that results were more reliable when the background flux was minimized, we subjected films to an outgassing cycle in an evacuated jar (i.e., a vacuum dessicator containing no dessicant) at 50 °C overnight. The vacuum was applied continuously with a mechanical pump using a liquid N<sub>2</sub> cold trap in the line. It was necessary to filter the air which was admitted to the dessicator before opening it. The films tended to attract dust and dirt from unfiltered air. An alpha particle source placed in the dessicator with the films reduced problems with static charges.

### 3. DATA COLLECTION FOR CERTIFICATE VALUES

It was decided to characterize the following properties of SRM 1470:

- 1) The permeance  $P(T_0, P_0)$ , at 23 °C and one atmosphere pressure differential,
- 2) The temperature coefficient of the permeance, and
- 3) The effect of pressure on permeance (if one was found).

The time-lag and its temperature and pressure dependence were also characterized. The range of values over which these were to be characterized was limited to that expected in the normal laboratory environment.

In order to characterize the above quantities it was necessary to subject each sample to a number of different levels of the variables in the experiment. We elected to use a 3 x 3 factorial design as shown in Table I. There are, therefore, nine different treatments to be applied to each sample. It is possible that the order in which the treatments are applied could alter the observations (through aging). Thus, there may be a need to randomize the order in which the treatments are applied.

Counterbalancing this need is the fact that the user of the film will generally be interested only in making his measurement under standard conditions (23 °C, 0.1013 MPa). For this reason, in our measurements we always applied the standard treatment first.

Table I

Treatment Schemes Used to Measure Certificate Values for SRM 1470

|                  | $T_0 - \Delta T$ | $T_0$ | $T_0 + \Delta T$ |          |
|------------------|------------------|-------|------------------|----------|
| $p_0 - \Delta p$ | 9                | 3     | 6                |          |
| $p_0$            | 7                | 1     | 4                | Scheme A |
| $p_0 + \Delta p$ | 8                | 2     | 5                |          |
|                  | $T_0 - \Delta T$ | $T_0$ | $T_0 + \Delta T$ |          |
| $p_0 - \Delta P$ | 6                | 3     | 9                |          |
| $p_0$            | 4                | 1     | 7                | Scheme B |
| $p_0 + \Delta p$ | 5                | 2     | 8                |          |

The second factor influencing the choice of the order in which treatments were to be applied was the fact that it was much easier to change the inlet pressure than to change the temperature. Thus, a particular temperature level was selected and the tests were carried out at the three different pressures before moving on to another temperature level. Complete randomization of the order of all treatments after the first, including the constraint that all three pressure levels had to be tested before moving on to a new temperature level, leads to 144 different orders in which to carry out the 8 measurements which remain.

It was felt that any effect of pressure on aging would be minimal. The order in which the pressure treatments were applied was, therefore, fixed. This reduced the number of treatment schemes to 2. Both schemes are shown in Table I.

True replication would require that the specimen be removed from the cell and reinserted between measurements. This was not practical in our case. In practice, however, a certain amount of replication was provided by repeating parts of a treatment sequence at a given temperature before going on to the next temperature. After enough data had been collected to characterize the temperature coefficient of permeance the measurement was further simplified by collecting only data from treatments 1, 2, and 3.

The NBS automated manometric permeation measuring facility and its operation are described in detail elsewhere [6]. An abbreviated description of the time-lag mode of operation used in these experiments is given below.

The specimen is first placed in a cell as shown in Figure 1. The fitted glass supports constrain the film and prevent distortion caused by an applied pressure gradient. The function of the microporous cellulose acetate cushions is to minimize damage to the film from loose glass particles or sharp edges in the cell. It is also thought that direct contact between the film and the impermeable glass of the rigid substrate may cause errors in the effective area through which the film is transmitting gas. The highly permeable cushion allows gas to diffuse away from the downstream side of the film before any localized excess of gas could accumulate.

After the specimen cell is connected into the measuring system, both the upstream (inlet) and the downstream (outlet) sides of the cell are evacuated. This provides an additional opportunity to eliminate gases sorbed in the film. The goal of removing all gases which could interfere with the measurement is never achieved. For this reason, the first step in the measuring process is to estimate the rate at which the film is outgassing. In order to accomplish this, the outlet side of the cell is isolated from the vacuum pumps while the inlet side of the cell remains under a vacuum. A small pressure rise, due to continued outgassing from the film, is observed in the measuring head. The apparent gas flux due to this source is measured. This flux is referred to as the "background" or "leakage" flux. Large values of the leakage flux often meant that the experiment was subject to a systematic error.

At an appropriate time (which is a new zero value for elapsed time) the gas pressure on the inlet side of the film is quickly raised to the value desired for measuring purposes. Pressure measurements on the outlet side of the membrane are made at closely spaced intervals



## CROSS SECTIONAL VIEW OF NBS SAMPLE CELL

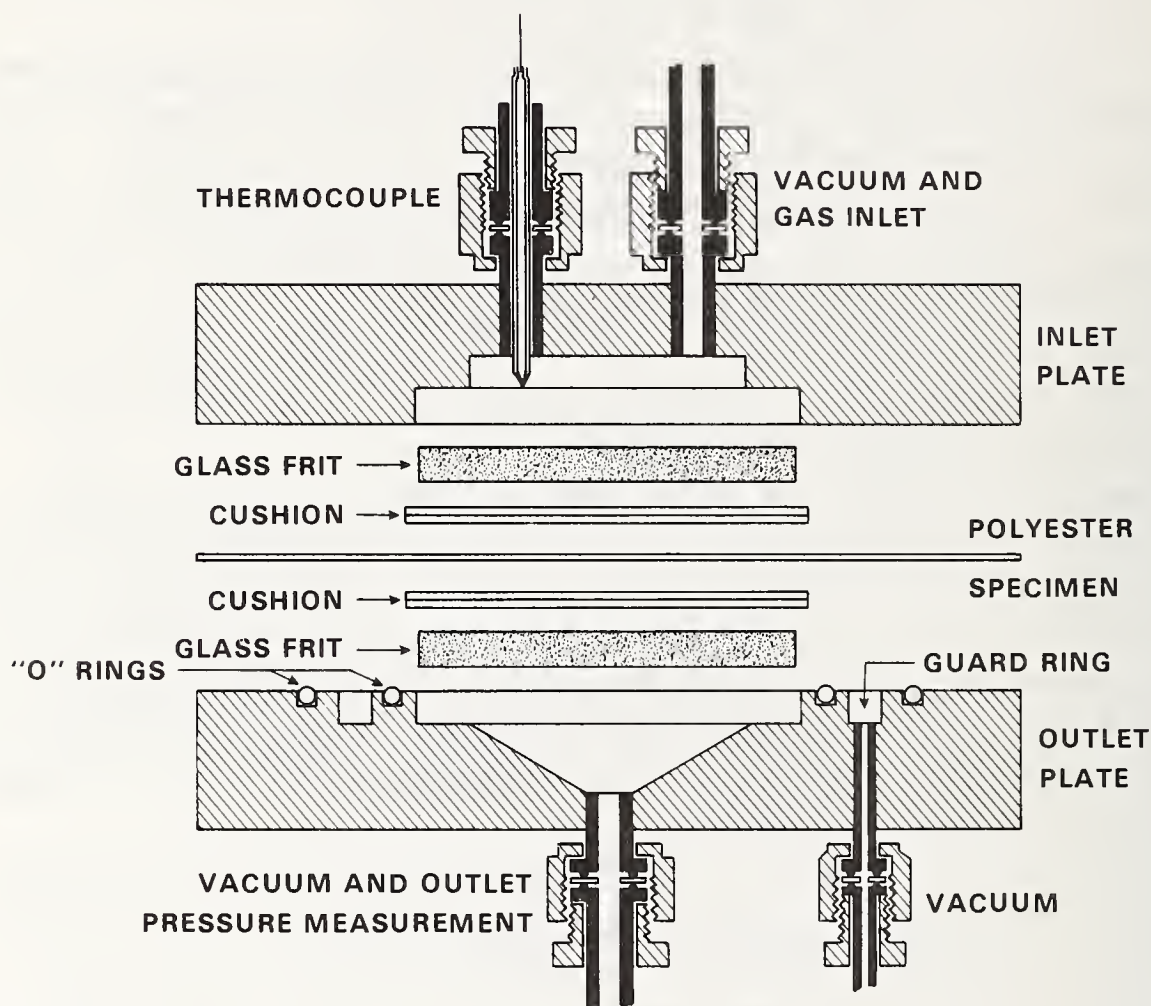


Figure 1. Cross Sectional View of NBS Sample Cell. This exploded view of the cell depicts the parts of the assembly that "sandwich" the specimen between the inlet (upstream) and outlet (downstream) chambers. The fritted glass supports provide necessary rigid support. The guard ring serves to trap gases that would otherwise enter the downstream chamber by leaking along the downstream face of the specimen.

until a time corresponding to 2 or 3 times the expected time-lag has elapsed. The interval between pressure measurements is then increased until the total elapsed time has exceeded the time-lag by a factor of 6 or 8. By this time the permeant flux will have attained a steady state. Values of pressure as a function of time were recorded on a magnetic tape cassette for subsequent computer analysis.

The analysis of the data consisted of extracting values of the permeance  $P$ , and the time-lag,  $\tau$ , from readings which had been corrected for background flux and calibration errors. An iterative nonlinear least squares technique was used.

The mean of the squared residuals between the model obtained by non-linear least-squares and the data was called  $\epsilon_{fit}$  and was used as a criterion for rejecting bad experimental runs. In all cases where  $\epsilon_{fit}$  was found to be greater than 0.3 Pa a systematic error was found in the raw data. In general it was found that the time-lag values from such sets of data were also meaningless.

Estimates of the errors in the parameters can also be obtained from the least-squares fits. Such estimates should be considered as measuring how well a given set of data fits the equation describing the pressure rise as a function of time. The precision with which  $P$  and  $\tau$  are determined on a given specimen is more properly assessed by replicate experiments.

#### 4. STATISTICAL ANALYSIS OF THE EXPERIMENTAL DATA

For the purpose of an SRM certificate, the experimentally determined quantities must be reduced to estimates of values which describe the whole population of possible values in terms of simple mathematical expressions.

##### 4.1 Models for Describing the Experimental Data

Since the steps which were taken to accomplish this were the same for measurements of both  $P$  and  $\tau$ , we will use the symbol  $Q$  to designate either one of these quantities in the ensuing discussion. We choose to label the specimen number by the symbol  $v$  and the experiment number by the index  $i$ . If the temperature during the  $i^{th}$  experiment is  $T$  and the pressure is  $p_j$ , where  $1 \leq j \leq 3$ , we can describe the result of a measurement by  $Q_i(T, p_j, v)$ . It is reasonable to describe the temperature influence by means of an activation energy:

$$Q(T, p, v) = Q(T_0, p, v) \exp \left[ \frac{E_A}{K} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (2)$$

With only three levels of the pressure available, it appears better to describe the pressure influence in terms of a discrete variable. The model used to describe the pressure effect is:

$$Q(T, p, v) = Q(T, \bar{p}, v) e^{\phi_j} \quad (3)$$

with  $\sum \phi_j \equiv 0$ . It is expected that  $\phi$  will be small. It is also expected that the influence of the specimen on  $Q(T, \bar{p}, v)$  can be represented by a deviation from a mean value which is a random function of  $v$ . This sample effect can be represented as:

$$Q(T, p, v) = \bar{Q}(T, p) e^{\beta_v} \quad (4)$$

where  $\sum \beta_v \equiv 0$ . The values of  $\phi_j$  and  $\beta_v$  are really coefficients of variation which measure the percentage variation due to the two effects. If we combine Eqs. 2, 3 and 4 and take the logarithms of both sides we can write our statistical model in the form:

$$\ln Q_i(T, p, v) = \mu(T_0, \bar{p}) + \beta_v + \phi_j + \frac{E_A}{RTT_0} (T - T_0) + \varepsilon_i \quad (5)$$

where  $\varepsilon_i$  is the random error in the observation. In Eq. 5 all interaction terms between factors have been omitted. A search was made for such effects but they were found to be negligible. Thus the  $\varepsilon_i$  may contain a contribution from the neglected interactions in addition to reflecting the random experimental error. The presence of the  $T - T_0$  term and the fact that the design is not balanced (due to the rejection or absence of some observations) led us to use multiple linear regression techniques [9] for obtaining estimates of  $\beta_v$ ,  $\phi_j$ , and  $E_A$  in Eq. 5. The vehicle used was the FIT command of the OMNITAB computer program [10]. The distribution of the residuals was examined and it was found that the  $\varepsilon_i$  were distributed normally.

#### 4.2 The Significance of the Regression Estimates

The parameter estimates derived from fitting the permeance and time-lag data to Eq. 5 are listed in Table II.

The units of  $e^{\mu+\phi_3}$  are  $\text{pmol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$  for the permeance and seconds for the time-lag. The activation energy  $E_A$  is given in  $\text{kJ/mol}$ . The quantities  $\phi$  and  $\beta$  are dimensionless.

The parameters  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  are the first parameters obtained from the regression analyses on the experimental data that we wish to discuss. Non-zero values of the  $\phi$ 's imply that there is a change in the permeability coefficient (or the time-lag) as the inlet pressure is changed. Indeed it appears that the permeance increases with increasing pressure ( $\phi_3 > \phi_2 > \phi_1$ ) while the time-lag is unaffected ( $\phi_j(\tau) \cong 0$ ).

The only mechanism known to produce a variation of  $P$  and  $\tau$  with pressure when one is considering dilute gases in semicrystalline polymers is partial immobilization [11]. If this mechanism were the source of the observed variation the trend of the  $\phi(P)$  would have to be reversed. It is also to be expected that  $\phi(\tau) \neq 0$  if partial immobilization is at work. Data of other workers [12] indicates that partial immobilization does not operate in the system  $\text{O}_2$  - PET. We are, therefore, left with the conclusion that partial immobilization is unlikely to be the source of the pressure effect on the permeance and the



Table II

Estimates from Multiple Linear Regression Analysis

| Parameter          | <u>Permeance</u> |                           | <u>Time-Lag</u> |                              |
|--------------------|------------------|---------------------------|-----------------|------------------------------|
|                    | Value            | Est. S.D.<br>( $S_K(P)$ ) | Value           | Est. S.D.<br>( $S_K(\tau)$ ) |
| $\mu(T_o, p_o)$    | -1.128           | 0.004                     | 5.840           | 0.006                        |
| $e\mu + \phi^3$    | 0.3302           | 0.0014                    | 343.8           | 1.9                          |
| $E_A$              | 27.2             | 0.3                       | -38.9           | 0.8                          |
| $\phi_1(p=.0872)$  | -.028            | .003                      | 0.000           | .007                         |
| $\phi_2(p=.1028)$  | .008             | .003                      | 0.000           | .007                         |
| $\phi_3(p=.1155)$  | .020             | .003                      | 0.000           | .007                         |
| $\hat{\beta}_1$    | -.050            | .009                      | -.029           | .022                         |
| $\hat{\beta}_2$    | -.007            | .009                      | .071            | .022                         |
| $\hat{\beta}_3$    | -.064            | .010                      | -.023           | .024                         |
| $\hat{\beta}_4$    | .027             | .011                      | -.002           | .026                         |
| $\hat{\beta}_5$    | -.004            | .011                      | -.001           | .026                         |
| $\hat{\beta}_6$    | .040             | .011                      | -.130           | .026                         |
| $\hat{\beta}_7$    | .025             | .009                      | -.028           | .020                         |
| $\hat{\beta}_8$    | .018             | .010                      | .010            | .023                         |
| $\hat{\beta}_9$    | -.042            | .010                      | .021            | .023                         |
| $\hat{\beta}_{10}$ | .025             | .009                      | .059            | .022                         |
| $\hat{\beta}_{11}$ | -.059            | .010                      | .065            | .023                         |
| $\hat{\beta}_{12}$ | .013             | .009                      | -.017           | .022                         |
| $\hat{\beta}_{13}$ | .019             | .010                      | .014            | .023                         |
| $\hat{\beta}_{14}$ | -.024            | .010                      | .027            | .023                         |
| $\hat{\beta}_{15}$ | .010             | .007                      | .011            | .016                         |
| $\hat{\beta}_{16}$ | .004             | .008                      | .034            | .019                         |
| $\hat{\beta}_{17}$ | -.025            | .008                      | .005            | .018                         |
| $\hat{\beta}_{18}$ | .028             | .016                      | -.040           | .039                         |
| $\hat{\beta}_{19}$ | .019             | .016                      | -.022           | .039                         |
| $\hat{\beta}_{20}$ | .038             | .014                      | .028            | .034                         |
| $\hat{\beta}_{21}$ | .029             | .012                      | -.011           | .028                         |
| $\hat{\beta}_{22}$ | -.020            | .013                      | -.013           | .031                         |

effect is, therefore, an artifact. The most likely source of this artifact is contamination of the upstream gas reservoir by  $N_2$  which leaks in (from the atmosphere along with  $O_2$ ) when the reservoir is evacuated and refilled. Confirmation for this interpretation is provided by the fact that the effect is also observed with He gas. The reservoir is being rebuilt to eliminate leakage and the operating pressure range of the system is being extended.

If contamination of the inlet reservoir is the source of the pressure effect  $P$  should approach its correct value asymptotically from below as  $p_{inlet}$  is raised. On this basis, the value  $e^{(\mu+\phi_3)}$  should be interpreted as the best (although biased) estimate for the permeability coefficient which can be derived from the present data. In any case, the  $\phi$  values represent a relatively small effect.

The values of permeance and diffusion constant found in this work are both lower than those observed by Michaels, et al. [13]. This indicates that SRM 1470 possesses a morphology which tends to impede the diffusion of oxygen molecules. This might be attributable either to crystallinity or to orientation.

The temperature effect is much more important than the pressure effect and considerable care should be taken to ascertain the temperature in any permeance measurement using SRM 1470. Differences between the experimental temperature,  $T$ , and the reference temperature,  $T_0$ , can be accounted for by means of the following equation:

$$Q(T) = Q(T_0) \exp \left\{ \frac{E_A}{RTT_0} (T - T_0) \right\} \quad (6)$$

The approximate temperature interval over which  $E_A$  was obtained is from 288 K to 310 K. The use of Eq. 6 for correction outside this interval is not justified (see Section 5.2). The values of  $E_A$  found in this work are somewhat lower than those found by Michaels et al. [13]. Such differences are not too surprising because the specimen morphology is known to influence the activation energies.

#### 4.3 Specimen-to-Specimen Variability

The parameters  $\hat{\beta}_1$  through  $\hat{\beta}_{22}$  represent effects due to changing from one specimen to another. Thus, if all data are corrected for temperature and pressure effects, there would still be significant differences between data taken on different specimens. The source of these differences may be in differences in the physical state between specimens or in some uncontrolled feature of the experiment which varies from one specimen to another. Figures 2 and 3 are scatter diagrams for  $\hat{\beta}_y(P)$  and  $\hat{\beta}_y(\tau)$  respectively. While the scatter diagrams do not clearly demonstrate that the parameter values are significantly different from zero the appropriate  $F$  tests show that the  $\beta$  terms contribute significantly to reduction of variation. The absence of a trend in these plots suggests that there was no influence attributable to a systematic factor whose value changed during the course of the experiments. The plots in Figures 4 and 5 indicate that there was no systematic trend from one part of the lot of material to the other which would give rise to the observed

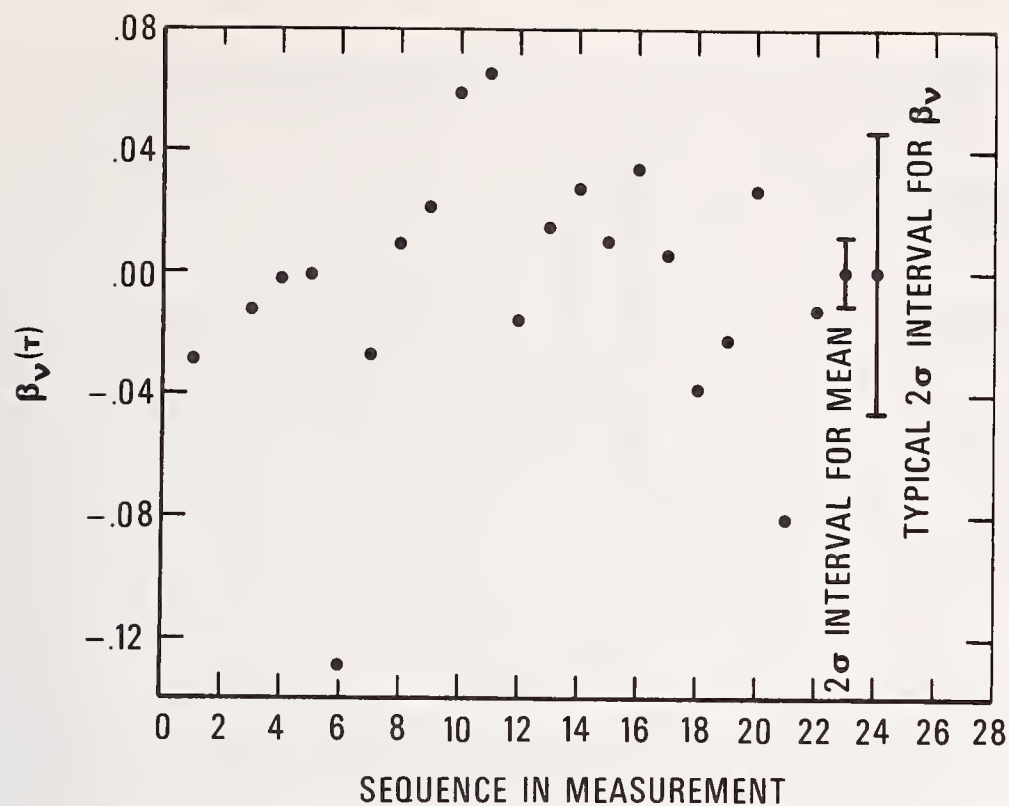


Figure 2. Scatter Diagram for the Specimen Effect on the Measured Permeance. The absence of a trend suggests that any cause of the specimen-to-specimen variability did not change during the sequence of measurements.

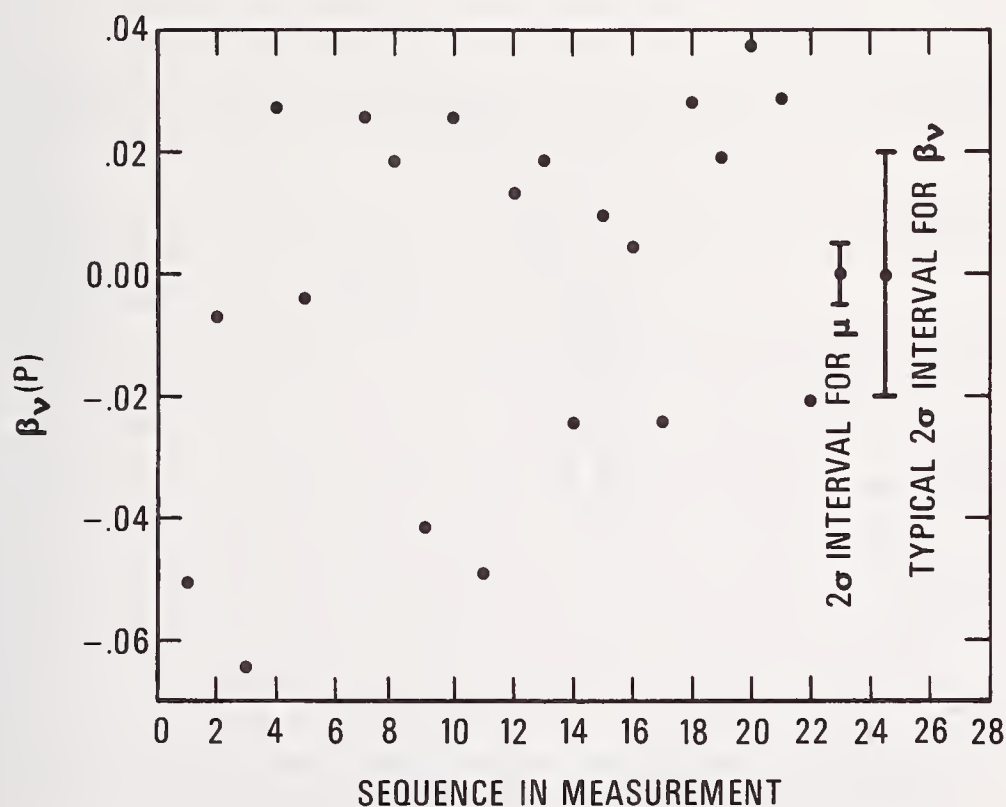


Figure 3. Scatter Diagram for the Specimen Effect on the Time-Lag. The absence of a trend suggests that no systematic changes were made in the technique for measuring the time-lag as the experiments progressed.



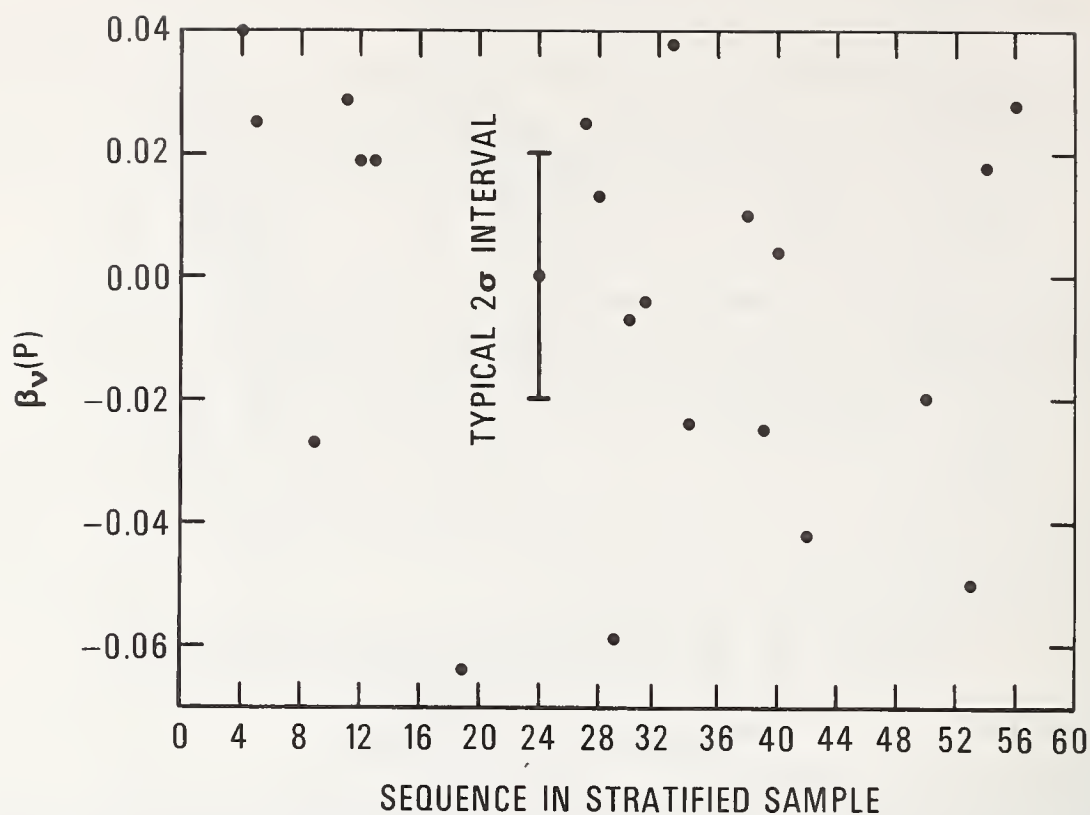


Figure 4. Scatter Diagram Giving Specimen Effect on the Permeance as a Function of Position Within the Stratified Sample. The absence of a trend indicates that properties do not change from one part of the batch of material to another.

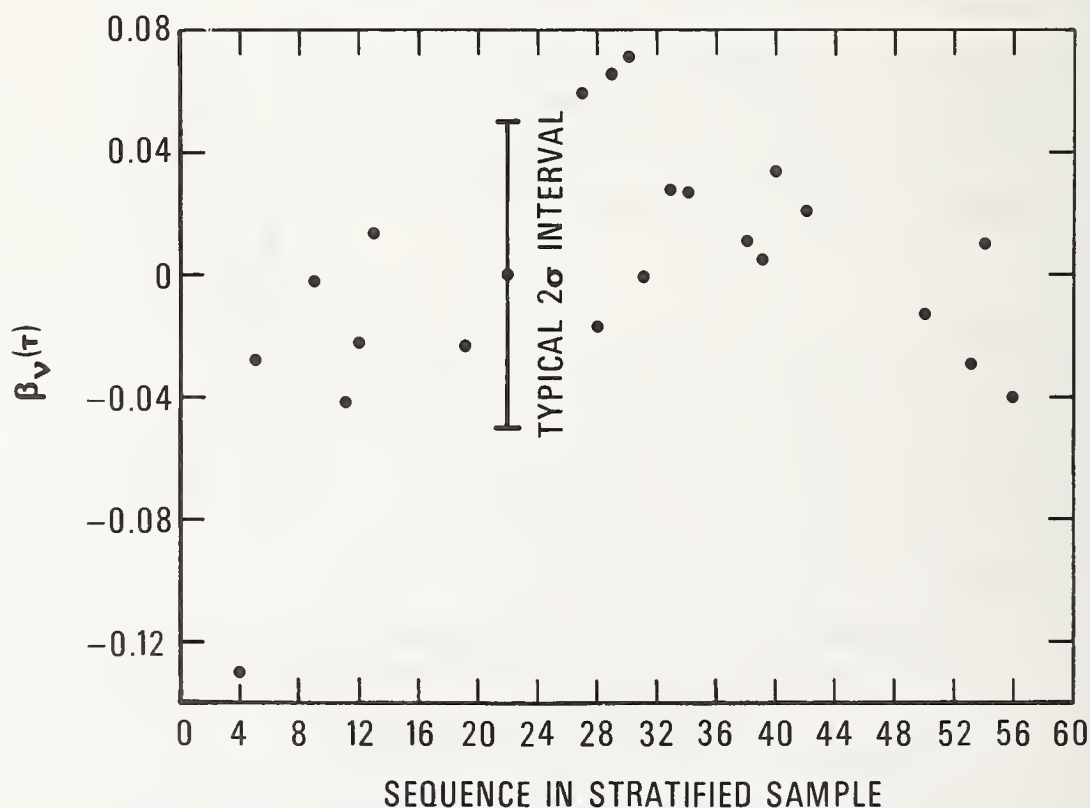


Figure 5. Scatter Diagram for Time-Lag Values as a Function of Position of the Specimen Within the Stratified Sample. The precision of the time-lag data is less than that of the permeance data. This accounts for the fact that more of the points fall within the two-sigma limits.

variation. The  $\beta_v$  are important because, as will be seen in Section 5.2, specimen-to-specimen variability is a primary source of differences among measurements made on SRM 1470. Since we do not now have a way of estimating  $\beta$  for a given specimen from additional characterization measurements we have to be content with treating the specimen-to-specimen effect as a random perturbation on the experimental measurements. It is reasonable to assume that the values of  $\beta$  are independent of one another and distributed normally with mean 0 and variance  $\sigma_\beta^2$  (we shall use the notation  $\beta \sim n(\mu, \sigma_\beta^2)$  to indicate that a random variable,  $\beta$  in this case, is normally distributed with mean  $\mu$  and variance  $\sigma^2$ ).

In order to construct tolerance intervals (see Section 5.2) we need to estimate  $\sigma_\beta^2$ . Now, if we recall that the  $\hat{\beta}$  in Table II are estimates (which contain a random error introduced by the estimation process) of the actual values of  $\beta$  we can write  $\hat{\beta}_v = \beta_v + \varepsilon_v$ , where  $\varepsilon$  is the random error of estimation. We can assume that  $\varepsilon \sim n(0, \sigma^2)$ . Thus  $\hat{\sigma}_\beta^2 = \sigma_\beta^2 - \sigma^2$ . The estimated standard deviations of the  $\hat{\beta}$  as derived from the regression analysis can be used to estimate  $\sigma^2$ . Note that the standard deviations all lie between 0.007 and 0.016, the larger values being derived from experiments using a truncated design (one temperature,  $T = T_0$ ). The observed values of  $\hat{\beta}$  form a sample of size 22 from the population of all sheets of film and the sample standard deviation can be estimated by  $S_\beta = \sqrt{\sum \hat{\beta}^2 / (n-1)} = 0.032$ . If we use 0.008 as a lower bound for  $\sigma$  then  $\sigma_\beta = [(0.032)^2 - (0.008)^2]^{1/2} = 0.031$  is an upper bound for  $\sigma_\beta$  from the permeance data. A similar analysis of the time-lag data yields  $\sigma_\beta(\tau) = 0.039$ .

It is reasonable to postulate that a portion of the specimen effect is attributable to manufacturing variability and another portion of this effect is attributable to random errors introduced in mounting the specimen in its holder. It is also possible that there are systematic differences from one cell to another which are not taken care of by the calibration step. Unfortunately the design of the present experiment confounds the three effects. The estimated variance of the sample effect appears to be consistent with what is known about the process for manufacturing PET film.

The  $\beta$  values do not seem to vary in any systematic way from one sample cell to another. It is, therefore, reasonable to discount any systematic cell-to-cell variability.

Given that the 15 sheets of film in a given can come from the same part of the original roll of film, one might hope that the specimen-to-specimen variability within a given can is lower than that over the lot as a whole. Unfortunately, it appears that two different sheets taken from the same can should be considered as two completely independent specimens. One basis for this statement is shown in Table III where we consider data from the cases where measurements were made on two samples from the same can. If the two measurements are considered as representative, the range  $R$  in Table III as determined from a random sample of size 2 can be used as an estimate of  $\sigma_\beta$  for the population of specimens in a single can. The fact that the mean value for the six observations of the range is not greatly less than the value of  $\sigma_\beta$  estimated above leads us to reject the hypothesis of reduced variation within a can.

The test described above is very crude and we have not attempted to estimate its power. A more detailed characterization of variability with respect to within-can and

within-lot components is prohibitive and the effort would be better spent improving the overall precision and seeking simple estimators for  $\beta(P)$  and  $\beta(\tau)$ .

In the analysis of the original experimental data, we found that cases where  $\beta(P)$  and  $\beta(\tau)$  both lay considerably outside the appropriate tolerance intervals were indicative of situations where pinholes were permitting anomalously high transmission through the membranes.

This observation led us to look for a correlation between  $\hat{\beta}_v(P)$  and  $\hat{\beta}_v(\tau)$ . If, for example, the specimen-to-specimen variability could be attributed to variations in thickness one would expect to find  $\hat{\beta}_v(\tau) \cong -2 \hat{\beta}_v(P)$ . The scatter diagram of Figure 6 shows that any such association between  $\beta_v(\tau)$  and  $\beta_v(P)$  is unlikely.

Table III  
Differences Between Samples from the Same Can

| CAN  | Permeability     |           |       | Time-Lag  |           |       |
|------|------------------|-----------|-------|-----------|-----------|-------|
|      | $\beta_\ell$     | $\beta_u$ | R     | $\beta_1$ | $\beta_u$ | R     |
| 234  | 0.019            | 0.029     | 0.010 | 0.041     | -0.022    | 0.019 |
| 524  | .013             | .025      | .012  | -.017     | .059      | .076  |
| 583  | -.059            | -.007     | .052  | .065      | .071      | .006  |
| 660  | -.024            | .038      | .062  | .027      | .028      | .001  |
| 785  | -.025            | .004      | .029  | .005      | .034      | .029  |
| 1080 | -.050            | .018      | .068  | -.029     | .010      | .039  |
|      | ( $\Sigma R$ )/6 | =         | .039  |           |           | .028  |
|      | $S_\beta$        |           | .031  |           |           | .039  |

Definitions: Let  $\beta_1$  and  $\beta_2$  be the result from measurements on two separate sheets from the same can of film. Then  $\beta_\ell = \min(\beta_1, \beta_2)$ ,  $\beta_u = \max(\beta_1, \beta_2)$ , and  $R = \beta_u - \beta_\ell$ .

The lack of precision of the  $\beta$  values renders attempts to find suitable estimators difficult. For example, a precision of better than one percent would be necessary if thickness measurements were to be used to develop estimates for  $\beta_v$  based on variability from this source. Thickness measurements with the needed precision are extremely difficult (if not impossible) to make on specimens 23  $\mu\text{m}$  in thickness.

Other quantities which should be investigated in an effort to develop estimators for  $\beta$  include density, crystallinity, and crystallite orientation. Experiments to investigate specimens with different morphologies are presently being prepared.

##### 5. THE ACCURACY OF THE MEAN VALUES OF P AND $\tau$

The extent to which parameters derived from the regression analysis represent accurate estimates of the true mean values of P and  $\tau$  is dependent on our success in providing



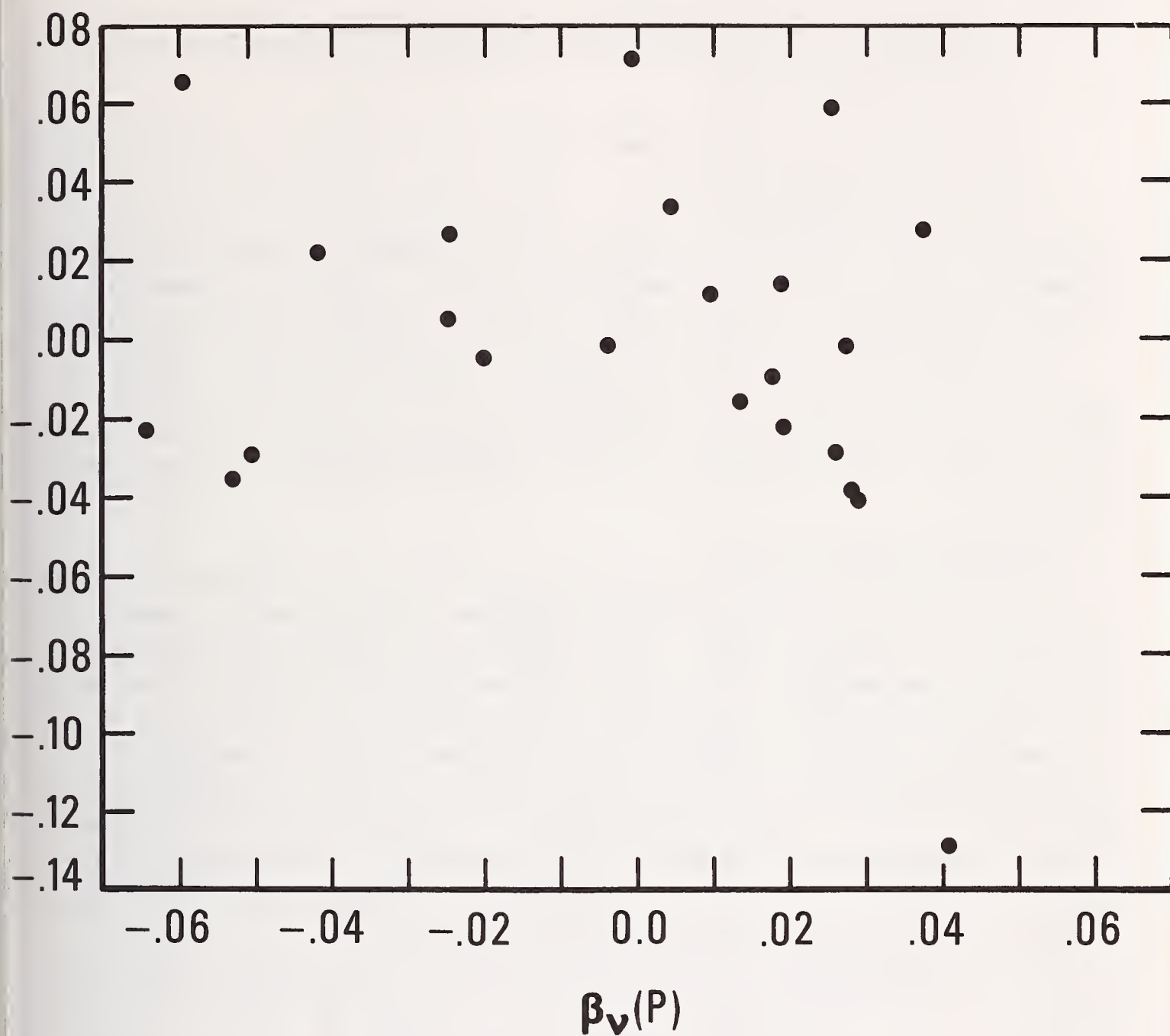


Figure 6. Correlation Plot of the Specimen Effect for Permeance Versus that for Time-Lag. The absence of clustering around a trend line suggests that these two properties are uncorrelated in any one piece of film.

traceability and eliminating bias. We have already pointed out that there is a possible bias in the P value due to  $N_2$  contamination of the upstream pressure reservoir. As far as is known, this is the only source of bias.

The permeance is a function of the following quantities which must be measured [6]:

1. The rate of pressure rise
2. The downstream cell volume
3. The effective area of gas transmission
4. The inlet reservoir pressure
5. The absolute temperature

A systematic error in any one of these quantities could introduce a bias into the results. The manner in which we have pursued these sources of error is discussed elsewhere [6]. For our present purposes it is sufficient to say that item 3 above is the most troublesome.

The time-lag values are subject to a somewhat different set of errors. Items 2, 3, and 4 do not influence the time-lag measurements. If the precision of the time-lag measurements could be improved and a similarly precise set of sorption measurements could be carried out it should be possible to make an independent determination of the effective area [14].

### 5.1 Variances of the Mean Values

The mean values quoted in Table IV represent the result of a large number of measurements carried out under carefully controlled conditions. Each of these measurements has a random error,  $\varepsilon$ , associated with it. This random error is  $\sim n(0, \sigma_\varepsilon^2)$ . Contributors to  $\sigma_e^2$  include random measurement errors in the instrumentation for recording data and controlling the experimental parameters. This source of error can, therefore, be expected to vary from one measuring facility to another. The best estimate of  $\sigma_e^2$  is the mean-squared residual which remains after fitting the model of Eq. 5 to the data (assuming that the model is not deficient in some systematic fashion). The mean values of  $\ln Q$  determined from our experiments differ from the true population means by a random amount which we assume is  $\sim n(0, \sigma_\mu^2)$ . The variance of  $\varepsilon_\mu$ ,  $\sigma_\mu^2 = V(\varepsilon_\mu)$ , is estimated by the square of  $S_\mu$  from the first line of Table IV. The relationship between  $\sigma_\mu^2$  and  $\sigma_e^2$  is  $\sigma_\mu^2 = \frac{\sigma_e^2}{N_{\text{eff}}}$ . The value of  $N_{\text{eff}}$  is less than  $N$ , the total number of measurements, because the

variance - covariance matrix is non-diagonal because of some factor, such as a lack of balance, in the statistical design of the experiment.  $N$  was 200 and  $N_{\text{eff}}$  was  $\cong 153$  for the data as presented.

Thus, in order to improve our estimates of the means we can take more measurements or reduce the error variance. The observed magnitudes of the error variances are consistent with estimates obtained by analyzing the variances of the contributing factors. This indicates that there is more to be gained from improving the precision and accuracy of the measuring apparatus than from improving the statistics.

### 5.2 The Use of SRM 1470 in Interlaboratory Comparisons

Facilitating interlaboratory comparisons of measurement methods and materials properties is certainly a primary objective of the Standard Reference Materials Program of the National Bureau of Standards [15]. In order to accomplish this goal, it is necessary to know what

Table IV

Quantities for Interlaboratory Comparisons

| Line | Quantity                                   | Symbol  | Permeability (P)  | Time-Lag ( $\tau$ )  |
|------|--|---|---|--|
| 1    | Mean of $\ln Q$                            | $\mu_Q(T_0)$  | -1.108  | 5.840  |
| 2    | Est. Standard Deviation of $\mu_Q$         | $S_\mu$   | .004  | .006   |
| 3    | Multiplier for $1-\alpha$ Confidence Limit | $Z_\alpha$  | $1.97(\alpha=0.05)$   | $1.97(\alpha=0.05)$  |
| 4    | Difference Between User and Certificate    | $\frac{E_A}{RTT_0} \Delta T + \beta + \varepsilon$                  | $11.06 \frac{\Delta T}{T} + \beta_p + \varepsilon_p$                      | $-15.80 \frac{\Delta T}{T} + \beta_\tau + \varepsilon_\tau$                    |
| 5    | Variance of User Measurement               | $(\Delta T)^2 \frac{V(E_A)}{(RTT_0)^2} + V(\beta) + V(\varepsilon)$ | $.0184 \left(\frac{\Delta T}{T}\right)^2 + V(\beta_p) + V(\varepsilon_p)$ | $.101 \left(\frac{\Delta T}{T}\right)^2 + V(\beta_\tau) + V(\varepsilon_\tau)$ |
| 6    | Variance Due to Specimen                   | $V(\beta) \cong S_\beta^2$  | $(.031)^2$  | $(.038)^2$   |
| 7    | Residual S.D. of Fit to NBS Data           | $S_\varepsilon \cong \sqrt{V(\varepsilon)}$                         | .030  | .069   |



quoted on SRM certificates mean and, perhaps even more important, what a measurement in a given laboratory actually estimates.

Table IV presents information which can be used for this purpose. The data on lines 1, 2, and 3 can be combined to give the usual confidence interval estimates in the form

$$\ln Q(T_0) = \mu_Q(T_0) \pm Z_\alpha S_\mu \quad (7)$$

For the present discussion, we have chosen to consider quantities which are natural logarithms of ones which are actually measured. This means that terms which are added to the logarithms are actually coefficients of variation and can be easily converted to percentages. The interval given by Eq. 7 is an interval within which the true value of  $\mu_Q(T_0)$  will be found  $100 \times (1-\alpha) \%$  of the time. The confidence interval represented by Eq. 7 above will generally not be approached by the average user of SRM 1470 because he is usually not prepared to make the large number of measurements on the large number of specimens that are necessary.

An experimenter who makes a measurement on a sheet of SRM 1470 can expect to obtain a permeance value (or a time-lag) which is different from the population mean value for four reasons:

- 1) his measurement temperature may be different from  $T_0$  by an amount  $\Delta T$ ,
- 2) the specimen he tests is likely to have a non-zero value of  $\beta$ ,
- 3) his test method may have a built-in bias,
- 4) his measurement will contain some random error.

The first effect can be accounted for by using the measured activation energy to correct all readings to  $T = T_0$ . The second and third effects can only be accounted for by making measurements on a large number of sheets of film. A bias will be revealed as a non-zero value for the mean of  $\hat{\beta}$ . Contributions due to random experimental errors must, as usual, be estimated from replicate measurements. All of the above factors must be considered when a user asks whether his measurement falls within an acceptable tolerance interval (see Section 6). Recourse must be taken to the Analysis of Variance [16] to construct intervals for more complicated sequences of measurements involving replication and multiple specimens.

Measurements made close to  $T_0$  have minimum variance. The variance increase slowly as  $|\Delta T| > 0$  (at a  $\Delta T$  of 15 °C this term constitutes  $(0.016)^2$  to the overall variance). A much more important term, over which the experimenter has no control, is  $V(\beta)$ . We have seen earlier that this is a characteristic of the population of specimens. Indeed, this term is the limiting factor on interlaboratory comparisons because it is necessary to make measurements on a larger number of specimens in order to see if there is a bias present. Further work is needed to provide for greater uniformity in specimens for a gas transmission rate SRM. Alternatively, it may be possible to develop relationships which will permit us to use the results of other measurements, such as thickness or density, to predict values for  $\beta$ .

Table V

## Units Related to Permeability

| QUANTITY           | SI UNIT<br>(abbreviation)      | COMMON UNIT                   | CONVERSION FACTOR<br>(common to SI) |
|--------------------|--------------------------------|-------------------------------|-------------------------------------|
| Quantity of Matter | mole (mol)                     | cm <sup>3</sup> (STP)         | $4.462 \times 10^{-5}$              |
|                    |                                | gram                          | depends on molecular weight         |
|                    |                                | grain                         | depends on molecular weight         |
| Thickness          | meter (m)                      | centimeter                    | $1.000 \times 10^{-2}$              |
|                    |                                | mil                           | $2.540 \times 10^{-5}$              |
| Pressure           | pascal (Pa)                    | pound per square inch         | $6.895 \times 10^3$                 |
|                    |                                | atmosphere                    | $1.013 \times 10^5$                 |
|                    |                                | centimeter of mercury (cm Hg) | $1.333 \times 10^3$                 |
| Area               | square meter (m <sup>2</sup> ) | 100 square inches             | $6.452 \times 10^{-2}$              |
|                    |                                | square centimeter             | $1.000 \times 10^{-4}$              |
| Time               | second(s)                      | day                           | $8.640 \times 10^4$                 |

Example: A widely known unit of permeability is the barrer which is  $10^{-10}$  cm<sup>3</sup>(STP)/(cm s cm Hg).

The table above provides a series of conversion factors as follows:

$$\begin{aligned}
 1 \text{ barrer} &= 10^{-10} \times 4.462 \times 10^{-5} / (10^{-2} \times 1.000 \times 1.333 \times 10^3) \\
 &= 3.347 \times 10^{-16} \text{ mol/(m s Pa)} = .3347 \text{ fmol/(m s Pa)}
 \end{aligned}$$

where we have used the prefix for  $10^{-15}$  (femto or f) to eliminate unnecessary powers of 10.

One cause of results which are far outside the interval defined by Eq. 7 is pinholes in the specimen. Pinholes (if they are prominent enough) give rise to large values of  $P$ , low values of  $\tau$ , and large errors in fitting the time-lag model to the raw data. A user who encounters a reading of this kind should examine his data very carefully. Another test for pinholes is discussed in Section 8.

## 6. HOW TO USE THE CERTIFICATE VALUES FOR SRM 1470

Contacts with some of the first persons to use SRM 1470 indicate that there is some difficulty in adapting to the set of units we have specified on the certificate which

accompanies each purchase of SRM 1470 (see Appendix A). As noted in Section 7 of this report, we have taken a departure from existing unit systems. The following information is provided to help users make conversions from the units they use to SI.

$P(T,p)$  is the ratio between the oxygen flux across the barrier and the pressure difference (in oxygen partial pressure) which exists across the membrane during the measurement process. Most of the standard measurement techniques measure the amount of permeant which flows across a well-defined area in unit time. This rate of flow can be converted to a flux by normalizing the result to a unit area of membrane. It is this flux which we have designated as the gas transmission rate,  $G$ .

Table I in Appendix A is meant to be used for converting gas transmission rates among different unit systems. In order to use Table I in Appendix A it is first necessary to convert the result of the user's measurement to a gas transmission rate. On direct-indicating devices this step is taken care of by internal calibration devices. The gas transmission rate should then be divided by the partial pressure difference across the membrane to obtain the measured value of  $P(T,p)$ .

Example: A user measures a gas transmission rate of  $63.8 \text{ scc}/(\text{m}^2 \cdot 24 \text{ hr})$  on a direct-reading gas transmission device. The pressure difference is one atmosphere and the film is at a temperature of  $23^\circ\text{C}$ . Using Table I of Appendix A, we find that the conversion factor between  $\text{scc}/(\text{m}^2 \cdot 24 \text{ hr})$  and  $\text{pmol}/(\text{m}^2 \cdot \text{s})$  is  $0.5160 \times 10^3$ . If we remember that one atmosphere is  $0.1013 \times 10^6 \text{ Pa}$ , we find that

$$P(T,p) = \frac{63.8 \times 0.5160 \times 10^3}{0.1013 \times 10^6} = 0.325 \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$$

The example given above is appropriate to the coulometric method of detection [3], equations suitable for calculating  $P(T,p)$  using other measurement methods are cited in [6]. Those who have become accustomed to using units which are not found in Table I of Appendix A can derive appropriate conversion factors by using the base units listed in Table V and forming the appropriate functions of conversion factors between base units.

## 7. THE UNITS OF P

The usual textbook definition of permeability [5,18,19] treats it as a property of bulk material and defines as the product of  $D$  and  $S$ , which are properties which can be defined on a microscopic (or molecular) scale for any material.  $D$  has units of  $\text{m}^2/\text{s}$  and  $S$  has units of  $\text{mol}/(\text{m}^3 \cdot \text{Pa})$  so that the permeability,  $\underline{P}$ , (so designated in order to distinguish it from the  $P$  used elsewhere in this paper to designate the permeance) has units of  $\text{mol}/(\text{m} \cdot \text{Pa} \cdot \text{s})$ .  $P$  has units of  $\text{mol}/(\text{m}^2 \cdot \text{Pa} \cdot \text{s})$ . The extra power of  $m$  in the units for  $\underline{P}$  arises because  $\underline{P}$  refers to a unit thickness of material.

The choice between  $P$  and  $\underline{P}$  as a means of describing permeation data is largely a question of whether one wishes to characterize a material or a product made from a



material. If the product is made from a material which is homogeneous throughout and whose dimensions can be accurately measured then  $\underline{P}$  is a good way to express results which can be expected to be useful under a wide range of end-use conditions. The vagaries of polymer processing, on the other hand, are such that one cannot always be certain that a product, such as a thin film, is homogeneous nor can the thickness always be ascertained accurately. In the case of SRM 1470 normalizing the data to unit thickness would probably introduce more scatter into the results because of the difficulty of measuring the film thickness to better than 3 or 4 percent, which is the accuracy to which the permeation flux through a given film could be measured. Eq. 1 in Section 1 is the basis for determining  $\underline{P}$  and we see that the determination requires only that the ratio between the permeation flux and the pressure difference across the barrier be measured.

If one ignores units,  $\underline{P}$  is defined by:

$$\underline{P} = \frac{\text{quantity of matter}}{\text{unit area} \cdot \text{unit time} \cdot \text{unit pressure difference}} \quad (8)$$

Table V shows a variety of ways for expressing each of the quantities in Eq. 8. None of the customary sets of units for expressing permeabilities [19] conform to SI throughout. In particular the mole has not found wide acceptance as representing the quantity of matter. The ISO [20] went so far as to promulgate a new gas transmission unit whose units are  $\text{fm}/(\text{Pa} \cdot \text{s})$ . These units were obtained from our units for  $\underline{P}$  by cancelling  $\text{cm}^3(\text{STP})$  in the numerator of the expression against  $\text{m}^2$  in the denominator. It is clearly wrong to make such a cancellation and the confusion could easily have been avoided if the quantity of matter had been expressed correctly.

In our work the units in which  $\underline{P}$  is expressed are completely those of the System Internationale (SI) [21] and thus represent the metric way of expressing the results of measurements.

Appendix A contains a table which can be used to convert gas transmission rates among different sets of units. (See example in Section 6).

## 8. MISCELLANEOUS ASPECTS OF SRM 1470

In the following sections we present additional observations which may be of interest to purchasers of SRM 1470. The use of polymeric materials as standards of measurement is still in its infancy and a great deal remains to be learned about their properties when used in this way.

### 8.1 Effect of Thermal History ("Aging")

In order to see if irreversible changes could be caused by thermal treatment at temperatures below  $T_g$  a series of experiments were carried out as listed in Table VI. The specimens were not pretreated. Permeability measurements were carried out in an up and down temperature cycle beginning at 23 °C, going to 37 °C, back to 23 °C, up to 50 °C, and back to 23 °C. Measurements were made at a given temperature for 24 hrs. before going to the next temperature.

Table VI  
Effect of Thermal History on Permeability

| Expt No | Sample A |   |             | Sample B |   |             | Sample C |   |             |
|---------|----------|---|-------------|----------|---|-------------|----------|---|-------------|
|         | Temp     | p | $P(T_0, p)$ | Temp     | p | $P(T_0, p)$ | Temp     | p | $P(T_0, p)$ |
| 1       | 295.8K   | 1 | .379        | 296.3K   | 1 | .380        | 296.9K   | 1 | .370        |
| 2       |          | 2 | .386        |          | 2 | .383        |          | 2 | .372        |
| 3       |          | 3 | .375        |          | 3 | .370        |          |   |             |
| 4       | 310.9K   | 1 | .384        | 310.9K   | 1 | .385        | 310.9K   | 1 | .374        |
| 5       |          | 2 | .388        |          | 2 | .387        |          | 2 | .380        |
| 6       |          | 3 | .377        |          | 3 | .380        |          | 3 | .353        |
| 7       | 295.5K   | 1 | .384        | 295.9K   | 1 | .384        | 296.7K   | 1 | .371        |
| 8       |          | 2 | .388        |          | 2 | .386        |          | 2 | .364        |
| 9       |          | 3 | .387        |          | 3 | .377        |          | 3 | .344        |
| 10      |          | 1 | .384        |          | 1 | .386        |          |   |             |
| 11      | 323.2K   | 1 | .396        | 322.8K   | 1 | .398        | 322.1K   | 1 | .385        |
| 12      |          | 2 | .404        |          | 2 | .403        |          | 2 | .395        |
| 13      |          | 3 | .393        |          | 3 | .392        |          | 3 | .368        |
| 14      | 295.9K   | 1 | .400        | 296.4K   | 1 | .395        | 297.0K   | 1 | .385        |
| 15      |          | 2 | .399        |          | 2 | .395        |          | 2 | .386        |
| 16      |          | 3 | .397        |          | 3 | .389        |          | 3 | .355        |

$$\begin{aligned} p_1 &= .1028 \text{ MPa} \\ p_2 &= .1185 \text{ MPa} \\ p_3 &= .0872 \text{ MPa} \end{aligned}$$

Note:

Units of  $P(T_0, p)$  are  $\text{pmol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$

The results in Table VI have all been normalized to 23 °C ( $P(T_0, p)$ ) using the activation energy experimentally determined. There appears to be an increase of about .005 in the value of  $P(T_0, p)$  on first going from 23 °C to 37 °C. Upon going back to 23 °C the original value is recovered. Increasing the temperature to 50 °C gives rise to an increase of about 0.012 in  $P(T_0, p)$  which is retained upon lowering the temperature back to 23 °C. These changes are barely larger than our confidence interval on the mean value of  $P(T_0, p)$  but the repeatability of measurements on a single sample shown in Table VII is much better than this (on the order of 0.003) so that the changes noted above are probably real.

Table VII  
Effect of Thermal History on Time-Lag

| Expt<br>No | Sample A |   |                  | Sample B |   |                  | Sample C |   |                  |
|------------|----------|---|------------------|----------|---|------------------|----------|---|------------------|
|            | Temp     | p | $\tau_L(T_0, p)$ | Temp     | p | $\tau_L(T_0, p)$ | Temp     | p | $\tau_L(T_0, p)$ |
| 1          | 295.8K   | 1 | 379.             | 296.3K   | 1 | 359.             | 296.9K   | 1 | 379.             |
| 2          |          | 2 | 383.             |          | 2 | 342.             |          | 2 | 392.             |
| 3          |          | 3 | 363.             |          | 3 | 321.             |          |   |                  |
| 4          | 310.9K   | 1 | 356.             | 310.9K   | 1 | 328.             | 310.9K   | 1 | 355.             |
| 5          |          | 2 | 344.             |          | 2 | 325.             |          | 2 | 359.             |
| 6          |          | 3 | 349.             |          | 3 | 330.             |          | 3 | 351.             |
| 7          | 295.5K   | 1 | 359.             | 295.9K   | 1 | 379.             | 296.7K   | 1 | 339.             |
| 8          |          | 2 | 369.             |          | 2 | 371.             |          | 2 | 364.             |
| 9          |          | 3 | 372.             |          | 3 | 377.             |          | 3 | 351.             |
| 10         |          | 1 | 330.             |          | 1 | 364.             |          |   |                  |
| 11         | 323.2K   | 1 | 321.             | 322.8K   | 1 | 332.             | 322.1K   | 1 | 389.             |
| 12         |          | 2 | 323.             |          | 2 | 312.             |          | 2 | 325.             |
| 13         |          | 3 | 326.             |          | 3 | 322.             |          | 3 | 326.             |
| 14         | 295.9K   | 1 | 348.             | 296.4K   | 1 | 354.             | 297.0K   | 1 | 357.             |
| 15         |          | 2 | 349.             |          | 2 | 354.             |          | 2 | 358.             |
| 16         |          | 3 | 348.             |          | 3 | 357.             |          | 3 | 361.             |

$$\begin{aligned} p_1 &= .1028 \text{ MPa} \\ p_2 &= .1185 \text{ MPa} \\ p_3 &= .0872 \text{ MPa} \end{aligned}$$

Note:

Units of  $\tau_L$  are seconds.

The time-lag data from these experiments (See Table VII) yield a mixed result when analyzed in the same way. This is probably due to scatter in the time-lag data. There is evidence that the morphology of the PET film changes with time (annealing) [8]. For this reason it is desirable to maintain the film as far below its glass transition temperature (see Section 8.3) as is practical. On the other hand refrigerating the film is not desirable because moisture could condense on cold films exposed to the atmosphere and lead to changes in permeability which may be more serious than those caused by aging at 23 °C. The aging effect of long-term storage at room temperature remains to be evaluated.

## 8.2 Significance of the Leakage Flux

The leakage flux decreases with time at a given temperature. This is evidence for an outgassing effect. Further proof that the leakage flux has its origins in outgassing from the film is provided by experiments in which the polyester film is replaced by an aluminum foil barrier. The pressure rise with the aluminum barrier in place is one fifth to one



tenth that found with the polyester film (in both experiments the upstream side of the cell is under a vacuum). Correlation of the leakage flux with other factors remain to be investigated.

The leakage flux is an important effect because its presence contributes to serious errors (as much as 10 to 20 percent) in the Linde Cell and Dow Cell procedures [22] which do not separate this flux from the true permeant flux. Experiments in which the outgassing species are trapped for subsequent analysis would be worthwhile. Some of the variation in the measured values of the time-lag and the permeability may be traceable to variations in outgassing behavior. The flux from outgassing species is not necessarily constant during the course of a given measurement and it is reasonable to believe that the correction for leakage flux (which assumes that the flux remains constant) is itself a source of error after a while.

It may be possible to eliminate some of the outgassing by proper conditioning of the film prior to measurement. It appears that the leakage flux is reduced if the film is measured at a low temperature after outgassing at a higher temperature. When choosing an outgassing temperature one must take care to ensure that the film is not annealed. In our experience a 24 hour outgassing at 50 °C did not prove to be too severe. It is also possible that a portion of the outgassing arises from degradation of the polymer to maintain an equilibrium between high and low molecular weight species. In this latter instance the effect is intrinsic to the polymer and cannot be eliminated.

### 8.3 Glass Transition Behavior in SRM 1470

In view of the fact that glassy polymers are known to undergo slow changes in thermodynamic state at temperatures below their glass transition temperature,  $T_g$  [8,23], we decided to try to characterize the glass transition behavior of SRM 1470. The results are shown in Figure 7. The curve labelled Q is for a sample which had been rapidly cooled after being melted and curve A is for a sample as received. Curve Q shows a well-developed glass transition region between 345 K and 360 K. There is also a prominent crystallization exotherm centered around 427 K. The area of this exotherm provides a measure of the amount of the material which is in the amorphous state. In curve A the crystallization feature is essentially absent and the feature associated with the glass transition is very weak. The evidence is that there is very little possibility for reorganization of the molecular chains.

This is not surprising in view of the relatively high crystallinity of the materials as revealed by its density (1396 kg/m<sup>3</sup>). It is also known that this material is biaxially cold-drawn when it is made. Both the drawing process and the crystallinity lead to constraints on the ability of the chains to reorient. On this basis we expect that SRM 1470 should be relatively immune to annealing effects in the temperature range of 23 °C to 50 °C. This temperature range represents the normal conditions which the film would be subjected to during postal shipment and conditioning prior to measurement.

### 8.4 Another Method for Assessing Pinholes

In earlier sections we have seen that pinholes in the films being tested manifest themselves through anomalous values of the time-lag and the permeability as well as through

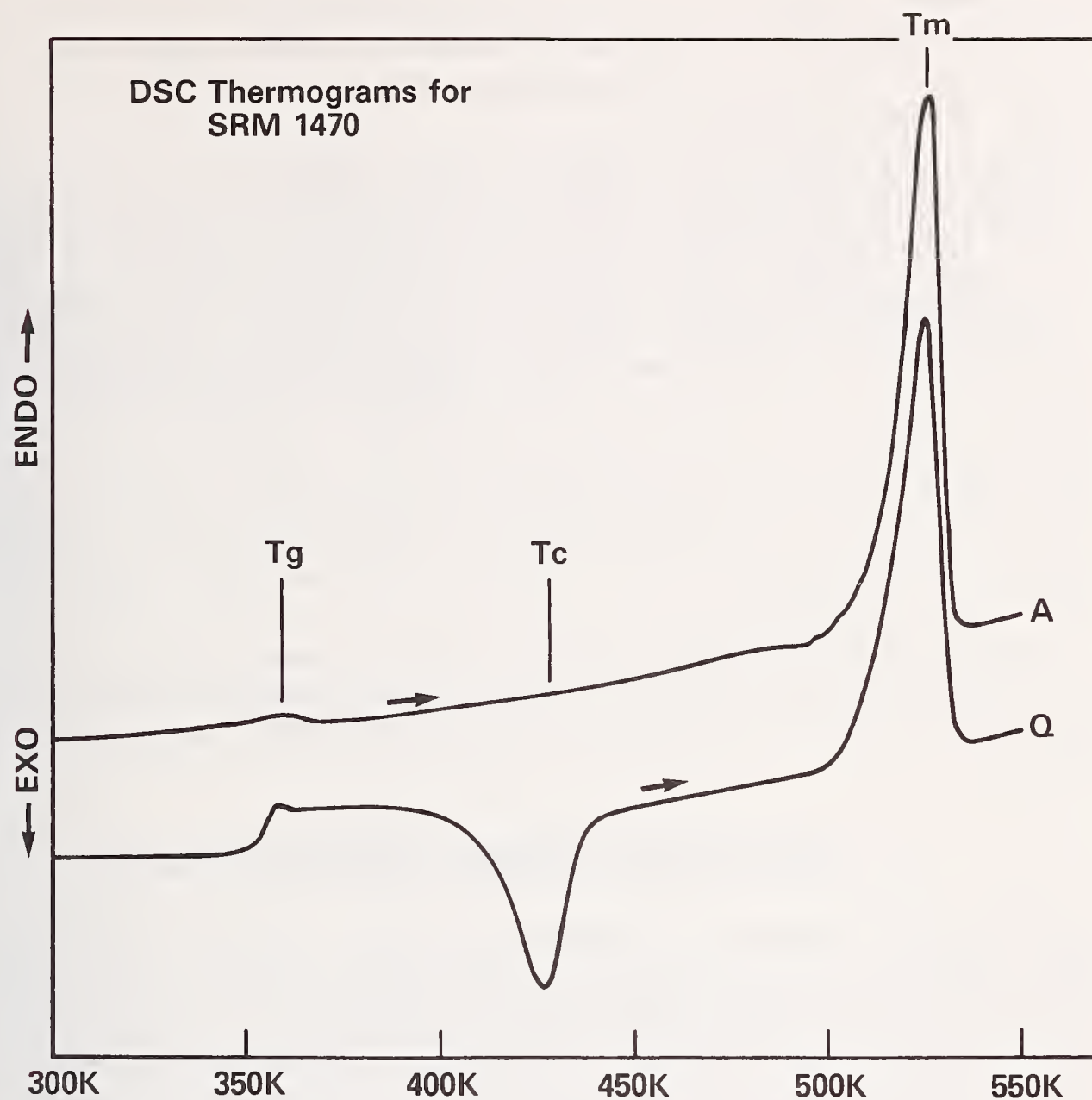


Figure 7. DSC (Differential Scanning Calorimetry) Thermogram for SRM 1470. The upper (A) trace was made on an as-received specimen of SRM 1470. The lower (Q) trace was made after specimen A had been cooled rapidly from above  $T_m$ .

poor fits between the theoretical curves and the experimental data. PET films are sensitive to mishandling. If a film is creased several pinholes will almost always appear. Ordinary care such as avoiding dirt particles and creases will almost always serve to keep pinholes away from the area being measured.

In spite of all precautions a pinhole will appear sooner or later. If a film is observed to have an exceptionally short time-lag and an exceptionally high transmission rate, it should be removed from the sample holder and checked for pinholes. A simple visual inspection sometimes reveals a crease or a prick mark on the film. These are the most likely locations for pinholes. Once the visual inspection is complete the film should be placed on a grounded aluminum plate. The surface of the plate should be smooth and free of projections. A hand-held Tesla coil should then be passed over the film far enough away from it so that no sparks penetrate the film. As the Tesla coil is moved closer to the film surface some small number of sparks will begin to penetrate the film. The locations where the sparks penetrate the film should be circled with a china-marking pencil for later examination. We have found that a pinhole was almost always in the vicinity of a preexisting flaw.

The technique described above is cheap and simple but somewhat subjective. It is easy to practice by using a sheet of film which has been deliberately creased or pricked. On a fresh film sparks will travel for 2 or 3 cm along the film to penetrate it at a pinhole.

## 9. CORRECTIONS FOR NON-STANDARD TEMPERATURE AND PRESSURE

Once the user's measurement is converted to SI units it can be corrected to the standard temperature by multiplying by  $\exp[-11.06(T-T_0)/T]$  (this expression is slightly more accurate than  $\exp[-0.038(T-T_0)]$  as shown on the certificate). We advise against using the pressure correction shown on the certificate (which was printed before we discovered that the pressure coefficient was an artifact). Once the user's measurement result is converted to SI and corrected to standard temperature it can be compared with the value given on the certificate. In Section 4.2 we stated that we feel that the correct value of the permeability coefficient is closer to  $0.330 \text{ pmol}/(\text{m}^2\text{s Pa})$ . This value was obtained with the pressure on the upstream gas reservoir above atmospheric pressure and is, therefore, less likely to be influenced by  $\text{N}_2$  leakage into the reservoir. With this change in the mean value the two-sided tolerance interval within which 95% of all measurements will fall with 95% probability [17] becomes  $0.330 \pm 0.028 \text{ pmol}/(\text{m}^2\text{s Pa})$ . This represents a variability of about 8 percent, which corresponds roughly to 2.7 times the standard deviation of the sample-to-sample variability,  $\beta$ . In order to obtain a better comparison of the performance of his measuring system the user will have to make measurements on a number of samples so that he can make comparisons between his own estimate of the population mean value of the permeability and the value given by the 95% confidence interval derived from our measurements ( $0.330 \pm 0.004 \text{ pmol}/(\text{m}^2\text{s Pa})$ ).



## 10. ACKNOWLEDGEMENTS

Many members of ASTM Committees F-2 (Flexible Barrier Materials) and D-20 (Plastics) assisted this work through their contributions of ideas, experience, and moral support. E. I. DuPont de Nemours and Company donated some 12,500 sheets of polyester film. Dr. D. H. Reneker of NBS was responsible for pointing the authors along the research path taken in this work. William P. Reed of the Office of Standard Reference Materials was a constant source of help and encouragement. .

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# National Bureau of Standards Certificate

## Standard Reference Material 1470

### Polyester Plastic Film for Oxygen Gas Transmission

John D. Barnes and Gordon M. Martin

This Standard Reference Material is intended for use in the measurement of the oxygen gas transmission rate of thin polymeric films using the manometric [1], volumetric [1], or coulometric [2] methods. The permeability coefficient ( $P$ ) at 0.10133 MPa (one standard atmosphere) and 296.15 K of 24 films selected at random was determined [3]. Of the 24 samples one was found to have pin holes. Of the remaining 23, one yielded a permeability coefficient which was incompatible with the other 22 and was not included in the calculations. From these determinations the following value for the permeability coefficient was established with the uncertainty estimated at the 95% confidence level:

$$P(T_0, p_0) = 0.325 \pm 0.004 \text{ pmol}/(\text{m}^2 \text{ s Pa})$$

A two-sided tolerance interval within which 95% of all measurement values will fall with 95% probability [4] is given by:

$$P(T_0, p_0) = 0.325 \pm 0.028 \text{ pmol}/(\text{m}^2 \text{ s Pa})$$

The experimental measurements were performed over a range of pressures between 0.085 and 0.117 MPa and over a range of temperatures between 291 and 302 K. Temperature and pressure coefficients ( $\beta\gamma$ ) of permeability were determined and can be used to calculate the permeability coefficient under conditions different from the standard ones by using:

$$P(T, p) = P(T_0, p_0) e^{\beta(T-T_0)} e^{\gamma(p-p_0)}$$

where  $T_0 = 296.15 \text{ K}$ ,  $p_0 = 0.10133 \text{ MPa}$ ,  $\beta = 3.80 \times 10^{-2}/\text{K}$ , and  $\gamma = 1.4 \times 10^{-6}/\text{Pa}$ . Extrapolation to other temperatures and pressures should be limited to the range of 290 to 305 K and .085 to .117 MPa, respectively. Values for the permeability coefficient extrapolated beyond these temperatures and pressures are not certified.

The gas transmission rate,  $G$ , is obtained by multiplying  $P(T, p)$  by  $p$  and has units of  $\text{pmol}/(\text{m}^2 \text{ s})$ . Table I lists some conversion factors between the various units commonly used to express  $G$ .

Table I

| G desired   | pmol/(m <sup>2</sup> s)  | cm <sup>3</sup> /(m <sup>2</sup> day) | (m <sup>3</sup> /(100 in <sup>2</sup> day) |
|---|--------------------------|---------------------------------------|--|
| G Given   | Multiply G Given by      |                                       |  |
| pmol/m <sup>-2</sup> /s <sup>-1</sup>               | 1.000                    | 0.1938 x 10 <sup>-2</sup>             | 1.2503 x 10 <sup>-4</sup>                  |
| *cm <sup>3</sup> /m <sup>-2</sup> day <sup>-1</sup> | 0.5160 x 10 <sup>3</sup> | 1.000                                 | 0.06452                                    |
| *cm <sup>3</sup> /100 in <sup>2</sup> /day          | 0.7998 x 10 <sup>4</sup> | 15.50                                 | 1.000                                      |

cm<sup>3</sup> - a cubic centimeter of gas at standard temperature and pressure (scg).

The overall coordination and evaluation of data leading to certification of this Standard Reference Material was performed by J. D. Barnes.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

## APPENDIX A (Cont'd.)

### USE and STORAGE

This Standard Reference Material has been carefully packaged to avoid damage, however, occasional pin holes or other defects may be present. If, during the measurement process, values outside the certified uncertainties are encountered, a new portion of the SRM should be used.

Measurements indicate this material to be stable when stored under normal laboratory conditions. Temperatures in excess of 50°C should be avoided. While long term stability of the SRM at room temperature has not been determined, it is being monitored. If the certified value changes beyond the stated uncertainty, NBS will notify purchasers.

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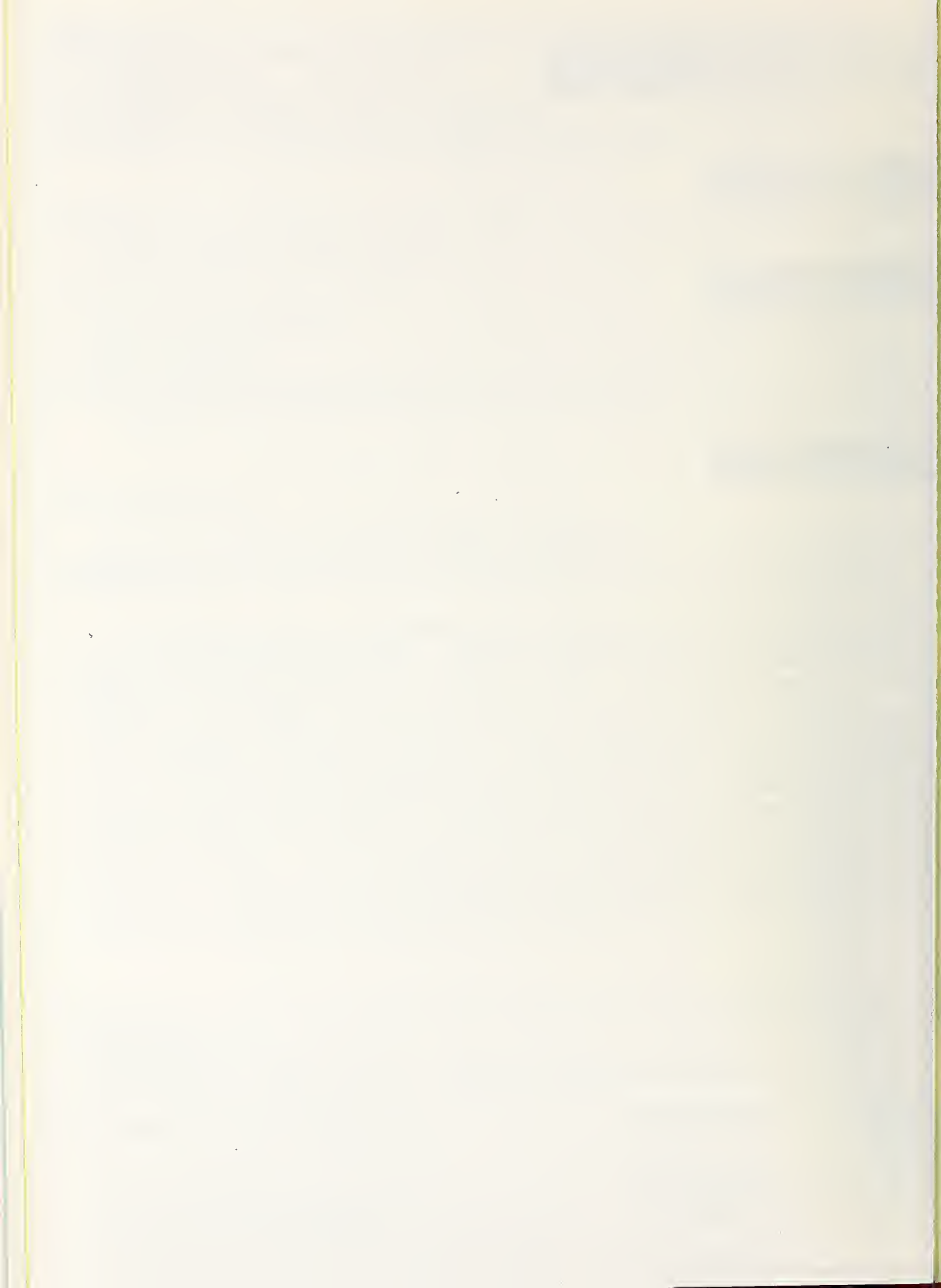
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| 16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)<br><br>This report presents information which should be of interest to users of NBS Standard Reference Material 1470. This SRM takes the form of 23 $\mu$ m thick sheets of poly(ethylene terephthalate) film. The gas transmission rates of these films with respect to oxygen gas have been carefully analyzed. We describe where the film comes from, how it is packaged, and how it should be conditioned prior to measuring. The steps which were taken to characterize a random sample of sheets from the production lot of the SRM are discussed in detail. The gas transmission rates and the time-lag of 22 films were measured using a state-of-the-art electronic manometric permeation facility. The temperature dependence of the permeability was determined over the temperature range 288 K to 310 K. A small pressure effect was found which is thought to be an artifact. The statistical measures which were derived from the data are discussed in detail. It is concluded that the largest source of variability is from one sample to another with a coefficient of variation amounting to 4 percent. A brief discussion of units for expressing permeabilities is given. Effects due to thermal conditioning ("aging") and outgassing are discussed. |   |  |                                   |
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